Study of the hydrolysis of the C=N bond in 3-phenyliminoxindol

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The hydrolysis of the C=N bond in the molecules of 3-phenyliminoxindol has been investigated polarographically in the medium of 0.1−1 N-NaOH. The effect of the concentration of catalytic particles as well as the effect of temperature on the overall reaction rate has been studied. The final products of hydrolysis have been isolated and identified.

In our preceding paper [1] the kinetics of the base hydrolysis of 3-(4-amino)phenyliminoxindol was studied. It was found that the hydrolysis yielded isatic acid and *p*-phenylenediamine and the individual polarographic waves of the reduction of this compound were interpreted.

In the present study it was shown that the slope of the wave of isatic acid changed with time during the base hydrolysis of 3-(4-amino)phenyliminoxindol. It was therefore necessary to ascribe this change to the formation of an unstable reaction intermediate which in the case of the hydrolysis of 3-phenyliminoxindol showed a cathodic half-wave potential sufficiently different from that of the cathodic reduction of isatic acid.

In alkaline solutions the polarographic reduction of 3-phenyliminoxindol manifests itself in three separate cathodic waves. The most positive cathodic wave decreases with time and corresponds [1, 4] to the reduction of the C=N bond ($E_{1/2} = -800$ mV/ /SCE). The second cathodic wave ($E_{1/2} \sim -1500$ mV/SCE) increases with the decreasing first wave until it reaches the value of the limiting current of the first cathodic wave. This state corresponds to the reduction of the C=O bond in the molecules of the final hydrolysis product. The cathodic wave with $E_{1/2} \sim -1600$ mV/ /SCE expresses the reduction of the unstable hydrolysis intermediate. It is obvious from the linear relationship between $\log i_0/i$ and time that the reaction studied is first order. The slope of this linear relationship increases with the concentration of NaOH and temperature.

There is also a linear relationship between $\log k$ and the concentration of NaOH. The dependence of the overall rate constants on temperature at various NaOH concentrations may be expressed by the following equations *(1—4)*

$$\log k = -5350(\pm 1.901)\frac{1}{T} + 13.948\ (\pm 0.0057), \qquad (1)$$

$$r = 0.998, \quad 0.1\ \text{N-NaOH}, \quad n = 20$$

$$\log k = -4640(\pm 1.760)\frac{1}{T} + 12.070(\pm 0.0053), \tag{2}$$
$$r = 0.998, \quad 0.33 \text{ N-NaOH}, \quad n = 20$$

$$\log k = -4500(\pm 2.481)\frac{1}{T} + 11.840\ (\pm 0.0314), \tag{3}$$
$$r = 0.996, \quad 0.6 \text{ N-NaOH}, \quad n = 19$$

$$\log k = -3950(\pm 1.709)\frac{1}{T} + 10.344(\pm 0.0051), \tag{4}$$
$$r = 0.997, \quad 1 \text{ N-NaOH}, \quad n = 25$$

where r is the correlation factor and n is the number of evaluated values. The dependence of the overall rate constants on the NaOH concentration may be expressed by eqns (5—10)

$$k = 1.30 \times 10^{-2}(\pm 1.5 \times 10^{-4})\, c_{\text{NaOH}} + 1.1 \times 10^{-3}(\pm 3 \times 10^{-4}), \tag{5}$$
$$r = 0.999, \quad 50°C, \quad n = 15$$

Table 1

Overall rate constants and half-times of the reactions of the 10^{-3} M solution of 3-phenyliminoxindol in approximately 20 volume % of ethanol, $\mu = 1$

t [°C]	0.1 N-NaOH		0.33 N-NaOH		0.6 N-NaOH		1 N-NaOH	
	$k \cdot 10^2$ [min⁻¹] $\frac{\text{exp}}{\text{calc}}$	$t_{1/2}$ [min] $\frac{\text{exp}}{\text{calc}}$	$k \cdot 10^2$ [min⁻¹] $\frac{\text{exp}}{\text{calc}}$	$t_{1/2}$ [min] $\frac{\text{exp}}{\text{calc}}$	$k \cdot 10^{-2}$ [min⁻¹] $\frac{\text{exp}}{\text{calc}}$	$t_{1/2}$ [min] $\frac{\text{exp}}{\text{calc}}$	$k \ 10^2$ [min⁻¹] $\frac{\text{exp}}{\text{calc}}$	$t_{1/2}$ [min] $\frac{\text{exp}}{\text{calc}}$
50	0.27	261	0.54	128	0.84	82.2	1.14	48.5
	0.25	268	0.51	133	0.78	87.3	1.34	50.7
55	0.44	158	0.83	85.1	1.15	60.4	2.00	34.7
	0.45	155	0.85	82.6	1.27	55.0	2.06	33.8
60	0.74	94.1	1.29	53.9	1.92	36.2	2.95	23.5
	0.79	89.9	1.38	51.3	2.04	34.7	3.13	22.6
65	1.38	50.5	2.22	31.8	3.51	19.7	4.74	14.7
	1.36	52.0	2.22	31.8	3.23	21.9	4.68	15.1
70	2.44	28.7	3.50	20.0	5.17	13.3	6.63	10.4
	2.32	30.1	3.52	19.8	5.05	13.8	6.93	10.1
75	3.88	18.2	5.82	11.9	7.64	9.1	10.7	6.6
	3.88	18.2	5.61	12.3	7.80	8.7	10.1	6.7

k_{exp} — overall rate constants calculated from the arithmetic mean of the values,
k_{calc} — overall rate constants obtained after smoothing by the method of least squares.
Half-times of the hydrolysis are denoted by the symbol $t_{1/2}$.
Overall rate constants were calculated from the Arrhenius equation.

Table 2

Activation parameters of the overall reaction $c = 10^{-3}$ M, 20 volume % of ethanol, $\mu = 1$
Activation parameters have been calculated according to [3]

Medium	E_a [kcal mol^{-1}]	A_0 [s^{-1}]	$\Delta S^{\neq}$ [cal mol^{-1} K^{-1}]
0.1 N-NaOH	24.5	1.5×10^{12}	-5.1
0.33 N-NaOH	21.1	2.0×10^{10}	-13.7
0.6 N-NaOH	20.6	1.1×10^{10}	-14.9
1.0 N-NaOH	18.1	3.7×10^{8}	-21.6

$$k = 1.81 \times 10^{-2}(\pm 4.6 \times 10^{-4})\, c_{NaOH} + 2.1 \times 10^{-3}(\pm 1.05 \times 10^{-4}), \quad (6)$$
$$r = 0.988, \quad 55°C, \quad n = 13$$

$$k = -2.46 \times 10^{-2}(\pm 1.9 \times 10^{-4})\, c_{NaOH} + 4.8 \times 10^{-3}(\pm 1.2 \times 10^{-4}), \quad (7)$$
$$r = 0.999, \quad 60°C, \quad n = 16$$

$$k = 3.77 \times 10^{-2}(\pm 5.8 \times 10^{-4})\, c_{NaOH} + 1.03 \times 10^{-3}(\pm 3.5 \times 10^{-4}), \quad (8)$$
$$r = 0.996, \quad 65°C, \quad n = 15$$

$$k = 4.74 \times 10^{-2}(\pm 9.0 \times 10^{-4})\, c_{NaOH} + 2.03 \times 10^{-2}(\pm 5.8 \times 10^{-4}), \quad (9)$$
$$r = 0.993, \quad 70°C, \quad n = 13$$

$$k = 7.42 \times 10^{-2}(\pm 1.74 \times 10^{-3})\, c_{NaOH} + 3.22 \times 10^{-2}(\pm 1.18 \times 10^{-3}). \quad (10)$$
$$r = 0.998, \quad 75°C, \quad n = 14$$

The values of the overall rate constants as a function of temperature and NaOH concentration are listed in Table 1. The activation parameters of the overall reaction are given in Table 2. If the concentration of NaOH increases from the value of 0.1 to 1.0 N, the activation energy falls from 24.5 to 18.1 kcal mol^{-1}.

As evident from eqns (5—10), the values of the rate constants increase linearly with the concentration of sodium hydroxide. This relationship may be described by equation

$$k = k_1 + k_2\, c_{NaOH},$$

where k_1 expresses a contribution of the reaction catalyzed by water to the overall rate constant while $k_2\, c_{NaOH}$ is the contribution of the reaction catalyzed by OH$^-$ ions. Statistical evaluation of these effects is in Table 3. The temperature dependence of k_1 and k_2 is expressed by eqns (11) and (12)

$$\log k_1 = -6830(\pm 5.45)\,\frac{1}{T} + 18.19(\pm 1.6 \times 10^{-2}), \quad (11)$$

$$r = 0.997, \quad n = 6$$

$$\log k_2 = -3350(\pm 3.25)\,\frac{1}{T} + 8.48(\pm 1 \times 10^{-2}). \quad (12)$$

$$r = 0.997, \quad n = 6$$

Table 3

Rate constants of the non-catalyzed reaction k_1, catalytic coefficient k_2 ($k = k_1 +$ $+ k_2 c_{NaOH}$), and half-times of the hydrolysis of 3-phenyliminoxindol as a function of temperature

Concentration of the compound 10^{-3} M, 20 volume % of ethanol, $\mu = 1$

t [°C]	$k_1\ 10^2$ [min^{-1}]	$t_{1,1/2}$ [min]	$k_2 \cdot 10^2$ [min^{-1} mol^{-1}]	$t_{2,1/2}$ [min]
	$\dfrac{\text{exp}}{\text{calc}}$	$\dfrac{\text{exp}}{\text{calc}}$	$\dfrac{\text{exp}}{\text{calc}}$	$\dfrac{\text{exp}}{\text{calc}}$
50	0.11	632	1.30	53.5
	0.11	614	1.28	54.2
55	0.21	331	1.81	38.4
	0.23	306	1.81	38.4
60	0.40	145	2.46	28.3
	0.47	152	2.58	27.3
65	1.03	67.5	3.77	18.4
	0.95	75.6	3.64	19.4
70	2.03	34.2	4.74	14.7
	1.86	37.2	5.10	13.7
75	3.22	21.6	7.42	9.37
	3.60	18.7	7.00	9.73

It ensues from these results that the hydrolysis of the C=N bond in the molecules of 3-phenyliminoxindol is catalyzed by OH$^-$ ions as well as water molecules. The cathodic wave at about -1600 mV/SCE indicates the existence of an unstable hydrolysis intermediate. The hydrolysis of the C=N bonds in the molecules of Schiff bases catalyzed by H$^+$ ions also provides an unstable hydrolysis intermediate which has been detected by some authors [5—7].

The hydrolysis of 3-phenyliminoxindol is not a reversible reaction under the conditions used for our experiments. The rate-determining step is a decay of intermediates leading to final products. On the basis of these results as well as the results presented in paper [1] the reaction pathway may be described as follows

$$>C=N- + H_2O \xrightarrow[+OH^-]{} >C\overset{\overset{\displaystyle OH}{\vdots}}{\underset{}{\cdots}}N- \xrightarrow[-OH^-]{} >C=O + H_2N-$$
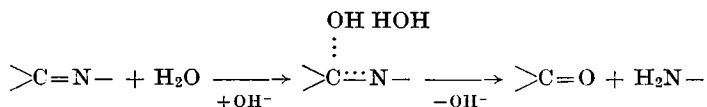
Experimental

The preparation of 3-phenyliminoxindol was performed according to [2]. After repeated crystallization in ethanol a compound of required purity with a sharp melting point was obtained. All other chemicals used were anal. grade.

For the hydrolysis of 3-phenyliminoxindol and identification of products the starting substance (0.5 g) was dissolved in the minimum possible volume of ethanol and poured

into a solution of 0.5 N-NaOH which contained 20 volume % of ethanol. The solution was kept at 60°C for 1 hr under constant stirring. Simultaneously it was checked polarographically. When the hydrolysis was complete, the solution was neutralized with hydrochloric acid and afterwards ethanol was distilled off under reduced pressure. The aqueous solution was extracted with benzene, which was evaporated and then the mixture was refluxed in ethanol containing 0.2 g of benzaldehyde and approximately 1 ml of pyridine. After about 60 min the mixture was concentrated and on cooling the crystals of the Schiff base $C_6H_5-CH=N-C_6H_5$ separated from solution. This compound was identified by mixed melting point and infrared spectrum. After acidifying to pH 1 and concentrating to one third of the original volume the crystals of isatin separated. This substance was identified by mixed melting point and R_F value using the thin Silufol layers (Kavalier, Votice) and a mixture consisting of $CHCl_3$ (70%) and benzene (30%).

The course of the hydrolysis of 3-phenyliminoxindol was investigated polarographically with an LP 7 (Laboratorní přístroje, Prague) polarograph. A thermostatted Kalousek vessel with separated saturated calomel electrode (SCE) was used. The temperature was kept constant (± 0.5°C) by means of a Hoeppler thermostat. The measurements were carried out in nitrogen atmosphere in alkaline solutions $0.1-1.0$ N-NaOH containing 20 volume % of n-propanol. An addition of KCl was used for adjusting the ionic strength to $\mu = 1$. The kinetic measurements were performed by recording continuously the height of the first decreasing cathodic wave at constant voltage as well as by recording the whole polarographic waves at certain time intervals.

The values of the overall rate constants k_{exp} as well as the regression coefficients were determined from the linear relationship between $\log i_0/i$ and time. The values k_{calc} presented in Table 1 were obtained by smoothing the function $\log k = f(1/T)$ by means of the method of least squares. All the values are the average of $3-5$ measurements. The calculation of activation energy E_a and frequency factor A_0 was based on the data obtained by applying the method of least squares to the Arrhenius equation. The increase in activation entropy $\Delta S^{\neq}$ was calculated according to [3].

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Translated by R. Domanský